Chemosphere 90 (2013) 796–804

Contents lists available at SciVerse ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Potential mobility of heavy metals through coupled application of sequential extraction and isotopic exchange: Comparison of leaching tests applied to soil and soakaway sediment

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HIGHLIGHTS

- ▶ Comparative study of heavy metal mobilization from soakaway sediment and soil.
- ▶ Integrated evaluation through fractionation, isotopic dilution and leaching test.
- ▶ Leaching tests showed gradual increase in isotopic exchangeability of metals.
- ▶ Rapid change in the free and labile complexes of metals except Pb.
- ▶ Intermittent flow condition seems to induce Cu retention but Zn & Pb leaching.

ARTICLE INFO

Article history:
Received 16 August 2012
Accepted 20 September 2012
Available online 1 November 2012

Keywords:
Column leaching
Heavy metal
Diffuse pollution
Artificial infiltration facilities
Groundwater contamination
Isotope dilution technique

ABSTRACT

Artificial infiltration facilities (AIFs) that enhance groundwater recharge and regulate urban runoff are going to be an integral element of the urban infrastructure. However, AIFs provide a sink which trap pollutants that are likely to cause groundwater contamination. The current study aimed first to examine the mobility characteristics of Cu, Zn, and Pb through soil and soakaway sediment using an integrated analytical approach for column leaching with artificial road runoff (ARR) and then to differentiate the sorption patterns among different samples, (i.e., surface soil, underlying soil, and soakaway sediments) using mass balances. In addition, the study compares metal retention and release under continuous and intermittent flow conditions. Column leaching experiments were conducted using batches for 10 and 30 d under continuous flow condition and for 20 d of intermittent leaching. Heavy metal content and partitioning in soil and sediment used in columns were well characterized before and after leaching experiments. The results showed that a gradual increase in pH and decrease in dissolved organic carbon had pronounced effect on the mobilization of heavy metals. Pb showed the highest retention compared to Cu and Zn which implies that metal complexes play a pivotal role in metal transport. Labile fractions were found to be trapped by the solid materials for retention and their high concentration in ARR is a major concern from the pollution point of view through infiltration facilities. Results obtained in this study predict the risk associated with the release of retained heavy metal under changing environmental conditions in AIFs.

1. Introduction

Rainwater harvesting has emerged as one of the most effective measures for sustainable urban water management. Artificial infiltration facilities (AIFs) are one of such measures that induce groundwater recharge, regulate storm water runoff and wet weather flow, and reduce the untreated water discharge to the river. However, AIF provides a sink that traps the road dust coming with storm water runoff (Datry et al., 2003; Murakami et al., 2009). Also, the urban road dust as well as runoff is widely known to contain persistent and toxic heavy metals especially Cu, Zn, and Pb (Banat et al., 2005; Bacon et al., 2006). This is why significant accumulation of heavy metals has been reported in trapped sediments (known as soakaway sediment) of AIFs. The heavy metals are likely to leach and cause groundwater contamination (Murakami et al., 2008a,b; Kumar et al., 2009).

Further, the trapped sediment remains in the AIF for long time, and is subjected to dynamic environmental conditions viz. temperature, alternate wet and dry period, chelating agents (Becker and

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http://dx.doi.org/10.1016/j.chemosphere.2012.09.082

Peiffer, 1997; Ashworth and Alloway, 2004), lowering of pH due to acid rain, creation of anoxic environment at the bottom of sediment, microbial degradation of organic matter (Datry et al., 2003), drying of sediment leading to enhanced oxidation of organic matter and weakening of adsorption of bonds (Saeki et al., 1993; Charlesworth and Lees, 1999). These governing factors with prominent effect on the inherent properties of the soakaway sediment can immensely affect heavy metal mobility and release from the AIF system (Murakami et al., 2008a).

It is widely reported that mobility of different metals depends on their speciation and the strength with which they are associated with different fractions (Teutsch et al., 2001; Bacon et al., 2006). However, sequential extraction schemes assuming equilibrium state are not the actual representation of field situation. It is also because extractants used for the partitioning lack the actual physico-chemical nature of road runoff such as pH, dissolved organic carbon, and major ions. Therefore, it is necessary to simulate the actual environmental scenario for metal leaching from AIFs through column experiment using an appropriate leachant.

There are several studies available in literature that used column leaching experiments to understand the leaching behavior of different metals in natural undisturbed soils (Camobreco et al., 1996) as well as disturbed soils/sediments (Van der Sloot et al., 1996; Murakami et al., 2008b). However, literature pertaining to the heavy metal leaching and retention through soakaway sediments is still very sparse. A comparison of the potential mobility of metals in soil and soakaway sediment is still lacking. This comparison can provide a linkage between the newer findings of soakaway sediment with the relatively rich literature of soil science.

Leaching behavior of heavy metals in porous medium is generally assessed through a mass balance between leaching solution and infiltrated leachates, without considering the change in metal speciation in the soil/sediment during leaching. Selective sequential dissolution (SSD) and isotopic dilution techniques (IDTs) are two most commonly applied techniques for the measurement of heavy metal speciation (Tiller et al., 1972; Nakhone and Young, 1993; Smolders et al., 1999; Tongtavee et al., 2005; Gonzalez et al., 2005; Kumar et al., 2010). Considering the advantages and disadvantages of both techniques the coupled application of the three-stage BCR protocol (proposed by the Community Bureau of Reference) and isotopically exchangeable metal concentrations (*E*-value) through isotopic tracers (^{65}Cu, ^{207}Pb and ^{66}Zn) is likely to give better insight into the heavy metal transport. Therefore, a detailed comparative study for soil and sediment, focusing on the illustration of mass balance, speciation and isotopic exchange, is still needed.

The present study aimed first to examine the mobility characteristics of Cu, Zn and Pb through soil and soakaway sediment using an integrated analytical approach for column leaching with artificial road runoff (ARR); and then to differentiate the sorption pattern among different samples, (i.e., surface soil, underlying soil, and soakaway sediments) using mass balance. In addition, metal retention and release under continuous and intermittent flow conditions were compared and the change in the labile metal concentration in receiving leachates was evaluated. Broadly, an attempt was made to understand the factors responsible for heavy metal mobilization through AIF for evaluating groundwater vulnerability from diffuse pollution sources.

2. Material and methods

Three types of samples viz. surface soil, underlying soil, (depth > 1.0 m), and soakaway sediment were used for this study. Soakaway sediment was collected from an AIF, Nerima ward, Tokyo. Two soil samples representing the surface soil and underlying soil were also collected from nearby recreational park at Nerima ward, Tokyo. Samples were characterized before and after column leaching test by determining the parameters like soil pH, moisture content, organic content, and cation exchange capacity (CEC) using standard methods (Topp, 1993; Kirel, 1993; Teutsch et al., 2001). The selected physico-chemical properties and metal contents of experimental samples have been provided as Supplement S1.

2.1. Soil column experiment

The columns used for the experiment were of poly vinyl chloride (PVC) with internal diameter of 30 mm and length of 150 mm. Columns were filled with 30 g of air dried and homogenized samples. The sample occupied about 6–7 cm of the length of the column. ARR was prepared in the laboratory using highway road dust and deionised water (DW) as a leachant to mimic actual condition of urban runoff received by AIF. DW and road dust were mixed in the ratio of 25 L kg^{-1} and stirred for 6 h at the speed of 250 rpm at 20 °C and left for settling. The supernatant obtained after 15 h of settling was regarded as the artificial road runoff (Murakami et al., 2008a,b; 2009) and fed into the columns in a down-flow mode. In order to simulate 10 mm h^{-1} of infiltration rate a flow rate of 0.12 mL min^{-1} was maintained by peristaltic pump. The leaching was performed under two different continuous and intermittent flow conditions. The flow volume under the continuous condition in one week of test mostly corresponded to one year of rainfall in Japan. Supplement 2 shows the chemical characteristics of ARR and Supplement 3 shows the validity of using ARR to mimic actual road runoff, where we have checked the four metal content of ARR with that of actual road runoff.

2.2. Experimental scheme

Leachates were collected on daily basis at the regular interval of 24 h (daily basis) and analyzed for pH, DOC (dissolved organic carbon), major ions (Na^+, K^+, Mg^{2+},Ca^{2+}, Cl^-, SO_4^{2-} and NO^{3-}) and heavy metals (Cu, Zn and Pb). Experiments were carried out in batch for 30 d under continuous flow conditions and for 20 d under intermittent flow conditions. An extra batch of columns operated for 10 d under continuous flow conditions was also installed to compare the results obtained for intermittent flow. This is because the amount of eluent passed through column under intermittent flow conditions for 20 d was equal to that under continuous flow mode for 10 d. At the end of the experiment each column sample was taken out, air dried and analyzed for heavy metal content, speciation and isotopic exchangeability to evaluate the change during the experiment. The entire column test was conducted at room temperature (20° ± 3 °C).

2.3. Chemical analyses

Total metal content in sediment and soil samples before and after leaching experiment was determined by ICPMS after digestion using microwave (Multiwave 3000, Anton Paar) using EPA method 3015a. The performance of the digestion technique was evaluated with certified reference material (CRM-8704, Buffalo River Sediment) which showed less than ±10% error in the recovery of total metal content. For speciation analysis, heavy metals (Cu, Zn and Pb) were fractionated according to BCR (Community Bureau of Reference) three-step sequential extraction procedure (Rauret et al., 1999). The first three fractions were exchangeable, reducible, and oxidisable which are operationally defined to be associated with carbonates, Fe/Mn oxides, and organic matter, respectively. The three steps are supposed to sequentially extract heavy metals in the order of decreasing mobility (Topp, 1993). In addition, the first three fractions of BCR which have potential to become mobile